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DEVELOPMENT OF HIGH STABILITY FUEL. EXECUTIVE SUMMARY.(U)

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DEVELOPMENT OF HIGH STABILITY FUEL

DEPARTMENT OF THE NAVY
NAVAL AIR PROPULSION TEST CENTER
CONTRACT N00140-74-C-0618

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EXECUTIVE SUMMARY

FEBRUARY, 1977

Exxon Research and Engineering Company, Government Research Laboratory, Linden, N. J.

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DEVELOPMENT OF HIGH STABILITY FUEL

EXECUTIVE SUMMARY

February 1977

By

William F. Taylor
and
John W. Frankenfeld

Exxon Research and Engineering Company
Government Research Laboratories
Linden, New Jersey 07036

Prepared Under Contract NO0140-74-C-0618

For

Department of the Navy
Naval Air Propulsion Test Center
Trenton, New Jersey 08628

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1. FOREWORD

This report contains an Executive Summary of the work done on the Development of High Stability Fuel program and was prepared by the Government Research Laboratories of Exxon Research and Engineering Company under Contract NO0140-74-C-0618 for the Department of the Navy. The contract was monitored by the Naval Air Propulsion Test Center, Trenton, New Jersey, by Mr. C. J. Nowack.

The overall program consisted of an initial analytical study entitled "Investigation and Analysis of Advanced Hydrocarbon Fluids" followed by an extended experimental effort entitled "Development of High Stability Fuel." Work on the program was carried out under the following Department of the Navy contracts:

- "Investigation and Analyses of Advanced Hydrocarbon Fluids", Contract N00019-70-C-0340, 15 December 1969 to 15 August 1970.
- "Development of High Stability Fuel", Contract N00019-71-C-0463, 5 April 1971 to 5 April 1972.
- "Development of High Stability Fuel", Contract NO0140-72-C-6892, 5 April 1972 to 5 October 1972.
- "Development of High Stability Fuel", Contract NO0140-73-C-0547, 6 October 1972 to 6 July 1973.
- "Development of High Stability Fuel", Contract NO0140-74-C-0618
 - Phase I 1 July 1974 to 31 December 1974
 - Phase II 1 April 1975 to 30 November 1975
 - Phase III 1 January 1976 to 30 November 1976

The principal investigators were Dr. William F. Taylor and Dr. John W. Frankenfeld assisted by Mr. A. W. Groman, Mr. W. Moss, and Mr. R. L. Bruncati. Other contributions were made by the following Exxon Research and Engineering Company personnel: W. G. Dukek, L. Berkowitz, D. Grafstein, A. Skopp and J. W. Harrison. Contributions were also made by the following Department of the Navy personnel: C. J. Nowack, L. Maggitti, Jr., J. R. Pichtelberger, K. H. Guttmann, E. A. Lichtman, and R. N. Hazlett.

2. EXECUTIVE SUMMARY

2.1 General Background

- Good thermal stability is a key requirement for aircraft turbine fuels.
- Petroleum derived fuels can degrade either while in storage or while being used in an aircraft fuel system. Deleterious sediments and/or deposits form as the end result of complex chemical and physical processes; and their rate of formation is determined both by the nature of the fuel itself and by the environment to which the fuel is exposed.
- The presence of dissolved oxygen in the fuel resulting from exposure to the atmosphere during normal handling and storage allows chemical reactions to occur (generally termed autoxidation) which play a major, if not dominant, role in fuel degradation. This fuel degradation can be accelerated by trace impurities and other harmful species present in the fuel, higher temperatures, and the presence of deleterious metals.

2.2 Program Background

- An assessment was made in the initial analytical study of the problem of finding a fuel capable of being exposed to temperatures near 1000°F (a temperature range representative of the most severe environment anticipated for a Mach 4.5 aircraft). Fuel stability was pinpointed as the key requirement of this fuel.
- Since present day JP-5 had inadequate thermal stability for this application, alternate routes to achieving this requirement were assessed. The use of cryogenics (such as liquified methane or hydrogen) as well as the use of pure chemical compounds was rejected.
- Instead it was proposed to develop the technology necessary to markedly improve the thermal stability of present JP-5 without significantly changing its composition. Such a High Stability JP-5 fuel offered significant advantages relative to the alternate possibilities in many areas such as cost, availability, simplified logistics and hazards suppression.
- A research program to develop High Stability JP-5 fuel was formulated and formed the basis for the experimental work which followed.

2.3 Program Approach

- A number of techniques were investigated which offered the possibility of markedly improving the thermal stability of JP-5 fuel without making a major change in its composition.
- Deposit formation rate measurements were made in an apparatus especially designed to simulate the severe environment anticipated for high speed flight (temperatures up to 1200°F and pressures up to 1000 psig).
- The principal approach was to investigate the improvement in thermal stability which would result from the removal of dissolved molecular oxygen. Fuels were deoxygenated from air saturated values of 50 to 80 PPM O_2 down to less than 1 PPM O_2 .
- The effect of fuel composition on stability in a deoxygenated system was investigated in detail because initial results indicated that fuel compositions could exert a strong effect on the magnitude of the improvement in thermal stability obtained with deoxygenation. In addition, other effects such as presence of dissolved metal, the nature of metal surfaces to which the fuel is exposed and the effect of present day additives, were investigated in a deoxygenated system.

2.4 Major Features of the Technology which was Developed

- High stability JP-5 can be achieved via a combination of deoxygenation (i.e. removal and/or exclusion of molecular oxygen) and control of the type and level of trace impurity compounds in the fuel.
- A rigorously deoxygenated (< 1 PPM O_2) High Stability JP-5 fuel can exhibit a fuel stability "breakpoint" temperature as high as 1100°F. Such a "breakpoint" temperature is believed to define the upper limit which is obtainable with hydrocarbon derived fuels.
- The deleterious compounds which must be removed or excluded from High Stability JP-5 represent a maximum of 5% of present day JP-5 compounds. High Stability JP-5 fuel, thus, is almost identical physically to present day JP-5 fuel.

- The deleterious compounds which must be controlled include:
 - The majority of the sulfur compound classes (4 out of 5 of the major classes of sulfur compounds potentially present in present day jet fuel).
 - Peroxides
 - Highly reactive olefins
- These deleterious compounds can be removed by catalytic hydrotreating of the fuel using present day technology.
- A number of classes of compounds should be left in the fuel as they appear to function as natural inhibitors which improve thermal stability. These compounds include one class of sulfur compounds (condensed thiophenes) and several classes of organic oxygen compounds (alcohols, esters and ketones).
- Although nitrogen compounds by themselves are not deleterious toward high temperature deposit formation in a deoxygenated fuel they can interact deleteriously with other trace impurity compounds and can also cause sediment formation problems at room temperature. This is not a major problem at present since petroleum derived jet fuels do not normally contain large quantities of nitrogen compounds. Nitrogen compounds may become a significant problem in the future, for example, when shale rock derived synthetic crudes are used which contain much higher levels of nitrogen.
- The non-olefinic hydrocarbons which comprise the majority of jet fuel compounds, i.e. paraffins, naphthenes and aromatics, are quite stable in a deoxygenated environment.
- Increasing the fuel pressure to levels higher than that presently employed does not increase the rate of deposit formation.
- The type and level of dissolved metals and the nature of the metal surfaces to which the fuel is exposed must be controlled.
- Not all present day additives are suitable for use in high stability fuel.
- Studies of the composition and morphology of the deposits produced in a deoxygenated fuel indicate that they are formed via different processes than deposits formed in an air saturated fuel.

2.5 Present Significance of This Technology

- Deoxygenation will generally improve the thermal stability of a JP-5 jet fuel.
- Present good quality jet fuels such as produced from a high quality virgin stock or from mildly hydrotreated poorer quality stocks should experience significantly improved thermal stability upon deoxygenation.
- Deoxygenation is an effective technique to improve the stability of JP-5 fuels in long term storage.
- When on-board nitrogen inerting systems are considered for aircraft for hazards suppression, than the concurrent use of deoxygenation to improve fuel thermal stability should also be considered as part of the system.
- A number of trace impurities should be excluded from fuels which require good storage or thermal stability, as they are harmful in the fuel regardless of whether the fuel is normally air saturated or deoxygenated.
 - The use of sweetening processes, which leave disulfided compounds or polysulfided compounds in certain cases in the fuel, should be avoided in preparing JP-5 fuel or fuel blending stocks, particularly in situations where storage or thermal stability is a problem.
 - The presence of peroxides and situations which tend to allow the formation of peroxides should be avoided.
 - The presence of highly reactive olefins which could occur from the use of thermally or catalytically cracked stocks without employing a subsequent catalytic hydrotreating step should be avoided.

2.6 Significance of This Technology for High Speed Aircraft

- The development of High Stability JP-5 fuel makes possible the design of a high speed aircraft which could use a fuel physically similar to present day JP-5 rather than a cryogenic fuel such as hydrogen or methane or an expensive pure chemical compound with limited availability.

- By markedly increasing the temperature to which a fuel can be exposed when used as a heat sink, High Stability JP-5 makes possible an improved high speed aircraft design, e.g. reduced weight of insulation giving improved performance for a given powerplant.

2.7 Significance In Relation to Future Synthetic Fuels

- The fuel technology developed in this program is based on a detailed understanding of the effect of the fuel's chemical composition on stability. Fuel technology developed in this form has fundamental, long term value since it is not derived from tests directly dependent on existing crude oil sources or state-of-the-art refining technology both of which may change with time. With such fuel technology, the effect on stability of changes in crude oil sources or changes in refining technology can be assessed by simply evaluating the effect of such changes on the chemical composition of the product fuel.
- A similar approach should be applied to the study of the stability of fuels derived from synthetic sources so as to develop a fuel stability technology base for alternate fuels. The development of such an understanding of the effect of synthetic fuel composition on stability is important because (1) stability will be more of a problem with synthetic fuels such as derived from shale oil than fuel derived from petroleum, particularly because of the much higher levels of nitrogen in shale crude oil, (2) present nitrogen removal technology requires very severe conditions to bring nitrogen levels in jet fuels derived from shale oil down to the very low levels presently found in petroleum derived fuels; and higher nitrogen levels will directionally degrade fuel stability, (3) even if better nitrogen removal technology is developed, e.g. improved catalytic hydrodenitrogenation processes, the higher cost of the additional hydrogen which will be required and the resultant loss of the energy efficiency of the overall processing system may preclude such drastic nitrogen removal and force a tradeoff to be made between reduced upgrading severity and increased nitrogen levels versus reduced product fuel storage and thermal stability properties.
- Deoxygenation may offer a means of improving the storage and thermal stability of synthetic fuels and this possibility should be assessed.

3. REFERENCES

The following reports and articles describe in detail the work which was carried out, the results and data which was obtained, and the analyses, conclusions, and recommendations derived from these results.

- W. F. Taylor, "Investigation and Analysis of Advanced Hydrocarbon Fluids" - Final Report, Volumes I and II, Contract NO0019-70-C-0340, GRX.2GAHF.71, August 1970.
- W. F. Taylor, "Development of High Stability Fuel" - Final Report, Contract NO0019-71-C-0463, GRX.6GAHF.72, April 1972.
- W. F. Taylor, "Development of High Stability Fuel" Semi-Annual Report, Contract NO0140-72-C-6892, October 1972.
- W. F. Taylor, "Development of High Stability Fuel", Nine Month Report, Contract NO0140-73-C-0547, GRUS.11GAHF.73, July 1973.
- W. F. Taylor and J. W. Frankenfeld, "Development of High Stability Fuel" Final Report for Phase I, Contract NO0140-74-C-0618, GRU.13GAHF.75, January 1975.
- W. F. Taylor and J. W. Frankenfeld, "Development of High Stability Fuel", Final Report for Phase II, Contract NO0140-74-C-0618, EXXON/GRU.15GAHF.75, December 1975.
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- W. F. Taylor, "Deposit Formation from Deoxygenated Hydrocarbons I General Features", Industrial and Engineering Chemistry Product Research and Development, Volume 13, Page 133-138 (1974).
- W. F. Taylor, "Deposit Formation for Deoxygenated Hydrocarbons II Effect of Trace Sulfur Compounds", Industrial and Engineering Chemistry Product Research and Development, Volume 15, Pages 64-67 (1976).

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